



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 419 254 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
24.06.1998 Bulletin 1998/26

(51) Int. Cl.⁶: **C08G 63/85**

(21) Application number: 90310292.9

(22) Date of filing: 20.09.1990

(54) Use of organotin esterification catalysts for reducing extractability

Verwendung von Organozinn-Esterifikationskatalysatoren zur Verringerung der Extrahierbarkeit

Utilisation de catalyseurs d'estérification à base de composés organoétain pour la réduction de l'extractibilité

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI NL SE

(30) Priority: 22.09.1989 US 411124

(43) Date of publication of application:
27.03.1991 Bulletin 1991/13

(73) Proprietor:
ELF ATOCHEM NORTH AMERICA, INC.
Philadelphia Pennsylvania 19102-3222 (US)

(72) Inventors:
• Larkin, William A.
Avon by the Sea, New Jersey 07717 (US)
• Bossert, Emily Carol
Westfield, New Jersey 07090 (US)
• Gibbon, Edmund M.
Somerset, New Jersey 08873 (US)

(74) Representative:
Stoner, Gerard Patrick et al
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

(56) References cited:
EP-A- 0 299 730 US-A- 2 720 507
US-A- 4 559 945

- RESEARCH DISCLOSURE. no. 283, November 1987, HAVANT GB pages 739 - 741; 'Polyesters With Good Extrusion Blow-Molding Characteristics.'
- CHEMICAL ABSTRACTS, vol. 112, no. 7, 12 February 1990, Columbus, Ohio, US; abstract no. 53897K, 'Indirect food additives; adhesives and components of coatings and polymers' page 600 ;
- DEUTSCHE LEBENSMITTEL-RUNDSCHAU vol. 68, no. 9, 1972, K. G. BERGNER UND H. BERG: 'Zur Migration einiger Zusatzstoffe aus Kunststoffen in Triglyceride im Vergleich zur Extrahierbarkeit durch organische Lösungsmittel.'

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 419 254 B1

Description

The present invention relates to the use of organotin esterification catalysts in the production of polyester and polyester-containing compositions for reducing extractability of catalyst components from a polyester article in contact with food, beverages, pharmaceuticals, or from a medical-device.

It is well known that organotin compositions, including organotin oxides, hydroxides, alkoxides and carboxylates, are effective as catalysts in the manufacture of polyester resins and polyester-containing compositions. The use of tin catalysts in the esterification of polyesters is discussed in US-A-2,720,507, 3,345,339, 4,554,344 4559945 and 2720501 and EP-A-299730 and Research Disclosure 28371. The organotin catalysts decrease the time required to complete esterification or transesterification and to effect complete reaction.

Polyester resins and compositions are useful in the manufacture of textiles, coatings, packaging and molded articles. A major application area is in the production of coatings and packages for storing and handling of foods, beverages, and pharmaceuticals and as components of medical devices. When used in such applications, the polyester compositions, and the articles made therefrom, need to be "non-toxic", that is, safe for use by consumers when used for their intended purpose. The compositions and their components generally require the approval of appropriate health-regulatory agencies, such as the U.S. Food and Drug Administration (USFDA). To obtain such approval, prospective users often have to conduct extensive tests, which are both time-consuming and expensive.

Organotin catalysts of the type employed herein have not yet been publicly sanctioned by the USFDA for use in the manufacture of polyesters intended for regulated "food-grade" (as defined by the USFDA) uses, such as food, beverage and pharmaceutical handling and packaging, or medical devices which come into contact with body fluids. Therefore, manufacturers of regulated food-grade polyester resins and polyester-containing compositions, as well as those who fabricate regulated articles therefrom, may resort to less-efficient catalysts or use no catalyst at all. However, the use of less-efficient catalysts, or no catalysts at all, can result in long reaction times with increased costs and energy consumption.

Some users have relied on the assumption that there is zero extraction of the catalyst from contact surfaces into foods, beverages, pharmaceuticals, and body fluids, and that therefore the catalyst is not a "food additive" (as defined by the USFDA), and requires no regulatory sanction. This is, however, an untenable position. Reliance on the assumption of zero extraction of the catalyst from such polyester articles without further testing is faulty, because the extractability of such catalysts from polyester articles into the wide variety of foods, beverages, pharmaceuticals, and body fluids with which they may come into contact is not known, particularly for articles intended for repeated use.

A more desirable situation is one in which the toxicity and extractability of the catalyst has been fully explored and reviewed by scientists experienced in chemistry, polymerization and toxicology so that a scientific judgment can be made and regulations can be published by the appropriate regulatory agency for general use by the public. Such regulations can state the composition of the catalyst material, the purity of the catalyst, the polyester resins and compositions in which the catalyst may be used, acceptable use levels of the catalyst, extraction testing procedures, and extraction limitations. Where the evidence submitted to the regulatory agency clearly demonstrates that the catalyst is of exceptionally low toxicity and only extractable in minute amounts under representative conditions of use in finished articles, the regulatory agency, for example, the USFDA, may conclude that the catalyst material may be used for its intended technical effect without requiring additional extraction testing by particular users, such as polyester manufacturers and article fabricators.

Aspects of the invention are set out in the claims.

Preferably, the non-toxic organotin catalysts used in the present invention have an LD₅₀ of at least 0.75 grams/kilogram (g/kg) when fed to rats, and an extractability from polyester and polyester-containing compositions and articles of not more than 200 ppb (billion = 10⁹) when extracted with water, corn oil, or heptane, using the procedures taught in Title 21 of the U.S. Code of Federal Regulations. In addition, the catalysts preferably have a triorganotin content of less than about 5 percent, and a heavy-metal content of less than about 200 parts per million (ppm). Furthermore, each component organotin compound has a purity of at least 90 percent.

The non-toxic organotin catalysts used in the present invention are suitable in the production of non-toxic polyester resins and compositions intended for contact with foods, beverages, and pharmaceuticals and in medical devices. The organotin catalysts are of sufficiently low toxicity, low extractability, and high purity to allow their use in such polyesters without further extraction testing by the users.

Polyester-containing articles are preferably in the form of coatings, bottles, packages, tubes, molded products, textiles, and film and sheet intended for packaging and handling foods, beverages, and pharmaceuticals, and for use in medical devices. The polyester article is characterized by extractability of the residual catalyst at levels acceptable to government regulatory agencies without resort to further extraction testing, typically 200 ppb or less.

The process for the manufacture of non-toxic polyester resins and polyester-containing compositions comprises the step of catalyzing a polyester esterification or transesterification reaction with the organotin catalysts described herein, leaving residual catalyst in the polyester article.

The organotin catalyst for preparing polyester resins is employed at a concentration of about 0.01 - 1.0 percent by weight (wt. %) based on the weight of polyester resin. (All percents herein are expressed as percents by weight, unless otherwise indicated.) A preferred concentration is about 0.05 - 0.2 wt. %. It may be advantageous to use a mixture of such catalysts. Therefore for purposes of this application, reference to "a catalyst" in accordance with this invention is intended to denote reference to one or more catalysts.

The organotin catalysts used in the present invention are hydroxybutyltin oxide (also known as butylstannoic acid), monobutyltin tris (2-ethylhexoate), and dibutyltin oxide.

The triorganotin content of the catalyst used in the present invention should preferably be less than about 5 percent. Triorganotin compounds are often undesirable byproducts in the manufacture of other organotin compounds. Because triorganotin compounds are generally considered toxic, their content in the catalyst should be minimized. Heavy metals are also undesirable impurities, and, therefore, the heavy-metal content of the catalyst is preferably less than about 200 parts per million (ppm).

Toxicity Studies:

The LD₅₀ test procedure was as follows:

Albino rats were administered the test materials by oral intubation. Following dosing, the rats were housed with food and water. Observations were made periodically during the first day and daily for fourteen days following. The results were as follows:

Test Material	LD ₅₀
Hydroxy butyltin oxide	>20 g/kg
Butyltin tris (2-ethylhexoate)	>3200 mg/kg
Dibutyltin oxide	>794 mg/kg

Extraction Studies:

Polyester resin was prepared from the reaction of isophthalic acid, maleic anhydride, propylene glycol and dipropylene glycol with and without tin catalysts. At the completion of the esterification reaction, the resin was diluted with styrene. Polyester plaques were prepared from these resins by addition of a peroxide to catalyze the reaction of the maleate unsaturation with styrene. Extraction studies were conducted using corn oil, water and heptane as the extractants.

The corn-oil extraction studies were carried out by exposing the plaques to corn oil at temperatures from -18°C to 190°C for 45 minutes. Organic matter in the oil extract was destroyed by acid digestion, and the amount of tin extracted was determined by atomic-absorption spectroscopy.

The water-extraction studies were carried out by exposure of cured plaques to water in a sealed vial at 190°C for three hours and at 160°C for ten days. The water extract was then analyzed for tin by atomic-absorption spectroscopy.

The heptane-extraction studies were carried out by exposure of the cured plaques to heptane at 130°C for two hours. The heptane extract was then analyzed for tin by atomic-absorption spectroscopy.

The results of the extraction studies are shown in Tables 1, 2, and 3 below.

TABLE 1

ANALYSES OF TIN EXTRACTED INTO OIL FROM CURED POLYESTER PLAQUES		
Catalyst	Tin in Resin (ppm)	Extracted Tin (ppb)
A	216	6
B	513	16
C	213	1
C	299	4
C	266	1

TABLE 1 (continued)

ANALYSES OF TIN EXTRACTED INTO OIL FROM CURED POLYESTER PLAQUES		
Catalyst	Tin in Resin (ppm)	Extracted Tin (ppb)
C	269	1
none	0	1
A = monobutyltin tris (2-ethylhexanoate) B = dibutyltin oxide C = hydroxybutyltin oxide		

TABLE 2

ANALYSES OF TIN EXTRACTED INTO WATER FROM CURED POLYESTER PLAQUES		
Catalyst	Tin in Resin (ppm)	Extracted Tin (ppb)
A	216	<1
B	513	27
C	213	3
C	299	3
C	266	1
C	269	<1
none	0	<1
A = monobutyltin tris (2-ethylhexanoate) B = dibutyltin oxide C = hydroxybutyltin oxide		

TABLE 3

ANALYSES OF TIN EXTRACTED INTO HEPTANE FROM CURED POLYESTER PLAQUES		
Catalyst	Tin in Resin (ppm)	Extracted Tin (ppb)
A	216	4
B	513	3
C	260	3
none	0	3
A = monobutyltin tris (2-ethylhexanoate) B = dibutyltin oxide C = hydroxybutyltin oxide		

While the inventors do not wish to be bound by any particular theory related to the surprisingly low extract-ability of these organotin catalysts, it is proposed that the minute quantities extracted, 200 ppb or less, may be due to conversion of these organotin catalysts containing at least one carbon-to-tin bond to inorganic tin compounds at the elevated tem-

perature at which the polyester is produced. Alternatively, these organotin catalysts containing at least one carbon-tin bond may be tightly bound in the polyester matrix either chemically or physically. Whatever mechanism is responsible, the minute extractability by oil, water and heptane make these catalysts suitable for use in non-toxic polyester-containing compositions intended for use in regulated food, beverage, pharmaceutical, and medical-device applications.

Polyester Definition

Polyesters used are generally the polycondensation product of one or more polyfunctional carboxylic acids, acid anhydrides, or esters with one or more polyhydroxyl alcohols. In addition there may be a monofunctional acid or alcohol end group.

Linear polyesters are prepared from the polycondensation of a dicarboxylic acid with a glycol. When a portion of the alcohol or acid components has a functionality greater than two, the structure may be cross-linked.

The acid and alcohol components may be aromatic, aliphatic, or mixed aromatic and aliphatic. Among the acceptable components are those listed in various USFDA regulations in Title 21 of the U.S. Code of Federal Regulations (CFR), including 21 CFR 177.2420 (a)(1), 21 CFR 175.300 (b)(3)(vii)(a) and (b), 21 CFR 175.320(b)(3), 21 CFR 176.170(a)(5) and (b)(2), 21 CFR 177.1590(a), 21 CFR 177.1660(a), and 21 CFR 177.1680(a)(2). In addition, monobasic acids, listed in 21 CFR 175.300 (b)(3)(vii)(b), may be used as chain stoppers.

In addition, the polyesters may be those described in 21 CFR 177.1240 and 21 CFR 177.1315.

The mole ratio of hydroxyl groups to acid groups theoretically is one to one; however, excess hydroxyl or acid groups may be used, depending on the end use of the polyester.

The tin catalysts are used in the esterification reaction in the manufacture of polyester resins. These resins may be used directly by thermoforming or may be cured by reaction with a cross-linking agent using an appropriate catalyst which may or may not contain tin.

Preferred polyesters for forming non-toxic compositions with tin catalysts include:

isophthalate-propylene glycol-maleate copolymer cured by reaction with styrene and peroxide-based catalyst;
polybutylene terephthalate;
polyethylene terephthalate; and
the reaction product of 2,2,4-trimethyl-1,3-pentanediol, trimethylol propane, isophthalic acid, and adipic acid cured with a cross-linking agent.

Examples of Catalyst Use in Resin Synthesis:

The importance of catalyst use in decreasing reaction time is illustrated by the following example:

Into a 2-liter, 3-neck reaction flask equipped with an N₂ inlet tube, air stirrer, pot thermometer, partial steam-heated condenser, and a receiver with full condenser, the following reagents were charged:

Propylene glycol	4.4 moles (334 g)
Isophthalic acid	2.0 moles (332 g)

The reaction mixture was heated to a maximum temperature of about 220°C, driving off the water of reaction. When the acid number, determined by titration with alcoholic KOH, reached approximately 10 milligrams KOH per gram (mg KOH/g) of sample, the reaction mass was cooled to about 160°C and 2.0 moles (196 g) of maleic anhydride was added.

The reaction mass was heated again to about 220°C and reaction continued, with removal of water, until the acid number reached 25 mg KOH/g sample.

A second reaction was carried out in the same manner, except that 0.86 g hydroxy monobutyltin oxide (MBTO) (0.20 mole % of initial charge) was added initially.

The reaction times for the two procedures are shown below:

Reaction Condition	First Stage Time in Hours	Second Stage Time in Hours
No catalyst	6.3	5.6

(continued)

Reaction Condition	First Stage Time in Hours	Second Stage Time in Hours
0.20 mole% MBTO	2.9	4.5

Similar reductions in reaction time were obtained in comparative tests using equivalent molar amounts of dibutyltin oxide and monobutyltin tris (2-ethylhexanoate) as the catalysts.

Synthesis of Typical Organotin Compounds:

Synthesis of organotin compounds is usually carried out by the condensation reaction of R_mSnCl_{4-m} with the acid or sodium salt of the desired OX groups, followed by washing with water and drying. Typical examples follow:

Dibutyltin oxide (DBTO):

Dibutyltin oxide is produced by the reaction of dibutyltin dichloride of at least 95% purity with an aqueous solution of sodium hydroxide. The product is washed with water, centrifuged, and dried. A yield of 99%, based on the dichloride charge, is expected. The purity is typically at least 95%, with less than 1% tributyltin oxide, less than 1.5% monobutyltin oxide, less than 1% moisture, and less than 200 ppm heavy metals.

Hydroxy monobutyltin oxide (MBTO):

MBTO is produced by the addition of an aqueous solution of monobutyltin trichloride of 95% purity to an aqueous solution of sodium hydroxide. The product is washed with water, centrifuged, and dried. A yield of about 95% is expected. The MBTO is generally at least 95% pure, with typical impurities including dibutyltin oxide, tributyltin oxide, moisture, and less than 200 ppm heavy metals.

Butyltin tris (2-ethylhexanoate):

Butyltin tris (2-ethylhexanoate) is produced by the reaction of aqueous monobutyltin trichloride of 95% purity with the sodium salt of 2-ethylhexanoic acid. The liquid product is separated, vacuum-stripped, cooled, and filtered. A yield of 98% is expected. The purity is typically at least 95%, with impurities including di- and tributyltin 2-ethylhexanoates, 2-ethylhexanoic acid, and less than 200 ppm heavy metals.

Claims

1. Use of an organotin catalyst comprising at least one of hydroxybutyltin oxide, monobutyltin tris(2-ethylhexanoate) and dibutyltin oxide, having a purity for said organotin compound(s) of at least 90 wt%, in the preparation of polyester or polyester-containing compositions for reducing extractability of catalyst components from a polyester article to be contacted with foods, beverages, or pharmaceuticals, or from a polyester-containing medical device.
2. Use according to claim 1 in which the organotin catalyst is used in an amount in the range from 0.05 to 0.2wt% based on the weight of polyester resin.
3. Use according to claim 1 or claim 2 in which the article or medical device is a coating, tank lining, film, sheet, fibre, bottle, package or moulded article.
4. Use according to claim 1 or claim 2 in which the article or medical device is a food can liner, bulk storage tank, beverage bottle, food wrap, blood bag, transfusion tubing or pharmaceutical packaging.

Patentansprüche

1. Verwendung eines Organozinnkatalysators, umfassend mindestens eines von Hydroxybutylzinnoxid, Monobutylzinntri-(2-ethylhexanoat) und Dibutylzinnoxid, mit einer Reinheit der genannten Organozinnverbindung(en) von mindestens 90 Gew.-%, zur Herstellung eines Polyesters oder von Polyester-enthaltenden Massen zur Verringerung der Extrahierbarkeit von Katalysatorkomponenten aus einem Polyestergegenstand, der mit Nahrungsmitteln, Getränken oder Arzneimitteln in Berührung kommt, oder aus einer einen Polyester-enthaltenden medizinischen

Vorrichtung.

2. Verwendung nach Anspruch 1, dadurch **gekennzeichnet**, daß der Organozinnkatalysator in einer Menge im Bereich von 0,05 bis 0,2 Gew.-%, bezogen auf das Gewicht des Polyesterharzes, verwendet wird.
3. Verwendung nach Anspruch 1 oder 2, dadurch **gekennzeichnet**, daß der Artikel oder die medizinische Vorrichtung eine Beschichtung, eine Tankauskleidung, ein Film, eine Folie, eine Faser, eine Flasche, eine Verpackung oder ein geformter Artikel ist.
4. Verwendung nach Anspruch 1 oder 2, dadurch **gekennzeichnet**, daß der Artikel oder die medizinische Vorrichtung eine Lebensmitteldosenauskleidung, ein großdimensionierter Lagertank, eine Getränkeflasche, eine Nahrungsmittelumhüllung, ein Blutbeutel, ein Transfusionsschlauch oder eine pharmazeutische Verpackung ist.

Revendications

1. Utilisation d'un catalyseur organique d'étain comprenant au moins un des composés consistant en oxyde d'hydroxybutylétain, tris (2-éthylhexanoate) de monobutylétain et oxyde de dibutylétain, ayant une pureté en ledit ou lesdits composés organiques d'étain d'au moins 90 % en poids, dans la préparation d'un polyester ou de compositions contenant un polyester pour réduire la capacité d'extraction de constituants catalytiques d'un article en polyester destiné à être mis en contact avec des aliments, des boissons ou des produits pharmaceutiques, ou d'un dispositif médical à base de polyester.
2. Utilisation suivant la revendication 1, dans laquelle le catalyseur organique d'étain est utilisé en une quantité de 0,05 à 0,2 % en poids sur la base du poids de la résine polyester.
3. Utilisation suivant la revendication 1 ou la revendication 2, dans laquelle l'article ou le dispositif médical est un revêtement, un revêtement de réservoir, un film, une feuille, une fibre, une bouteille, un emballage ou un article moulé.
4. Utilisation suivant la revendication 1 ou la revendication 2, dans laquelle l'article ou le dispositif médical est un revêtement de boîte de conserve, un réservoir de stockage de grand volume, une bouteille destinée à une boisson, un emballage alimentaire, une poche destinée à renfermer du sang, une tubulure de transfusion ou un emballage pharmaceutique.